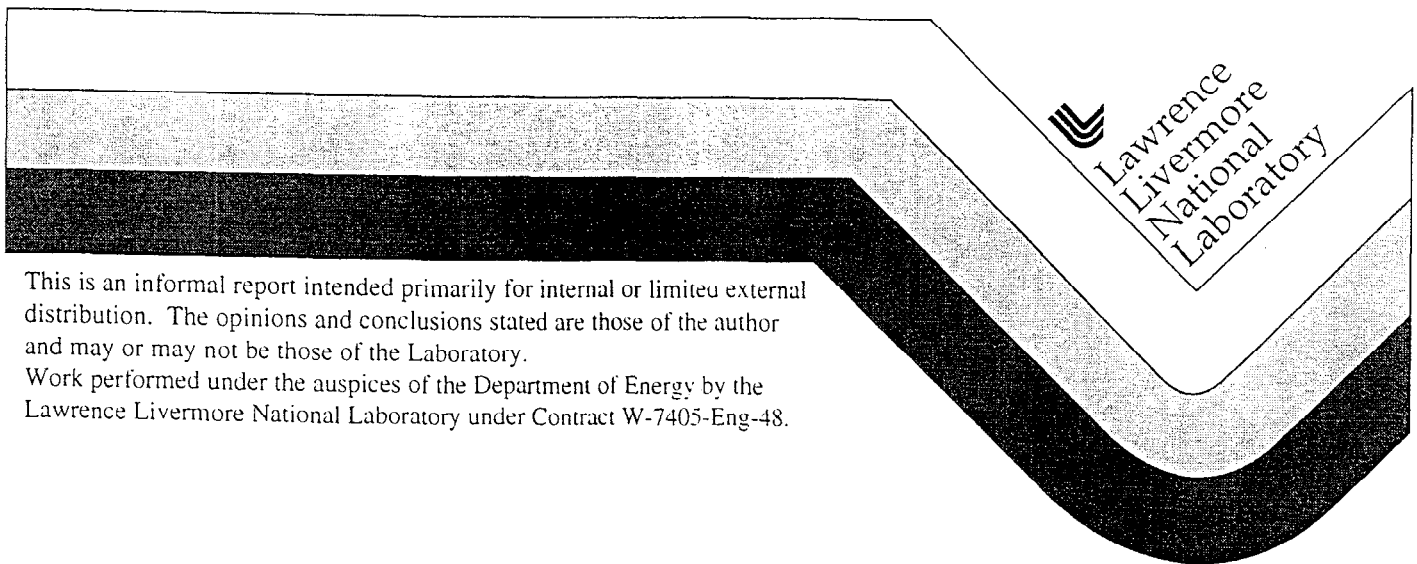


W1045 Environment on the Surfaces of the Drip Shield & Waste Package Outer Barrier

Gregory E. Gdowski

July 1999



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W1045 Environment on the Surfaces of the Drip Shield & Waste Package Outer Barrier

ANL-EBS-MD-000001, Rev. 00A

by Gregory E. Gdowski

July 1999

Lawrence Livermore National Laboratory
Livermore, California

OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT
ANALYSIS/MODEL COVER SHEET

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Page: 1 of 1

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ABBREVIATIONS AND ACRONYMS

DS	drip shield
a_0, a_1, a_3, a_4	experimentally determined constants for calculation of Henry's Law constant
Eh	electrochemical potential
EBS	engineered barrier system
$D_{O_2}(ppm)$	solubility of oxygen in parts per million (ppm) by weight
k	Henry's Law constant
MGR	monitored geologic repository
m	molality (moles of solute /1000 gm of solvent)
MW_{H_2O}	molecular weight of water (18.0153 gm/gm-mol)
MW_{O_2}	molecular weight of O ₂
M_{solute}	molarity (moles of the solute/liter of solution)
P_{total}	total pressure of the air
P^0	vapor pressure of pure substance
P	partial pressure
pH	negative logarithm of the hydrogen ion concentration
ppm	parts per million
RH	relative humidity ($P_{H_2O}/P_{H_2O}^0$)
QA	quality assurance
T	temperature (K)
x_{CO_2}	air fraction of carbon dioxide
x_{O_2}	air fraction of oxygen
x_{RH}	fractional relative humidity

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VP_{H_2O} water vapor pressure

ρ_{soln} density of the solution in gm/liter

WP waste package

WPOB waste package outer barrier

1. PURPOSE

These analyses provide information on the chemistry of the water films that form on drip shield (DS) and waste package outer barrier (WPOB) surfaces as a function of temperature, relative humidity, and gas phase composition. Water vapor is not included in the gas phase composition but is considered separately as the relative humidity. The analyses also provide information on the types of mineral/salt scale that could form on DS and WPOB surfaces. These analyses assume that the composition of in-drift water is similar to that of well J13 water or concentrated well J13 water. Well J13 water is assumed to be representative of the ambient conditions at the proposed repository horizon at Yucca Mountain, Nevada. The analyses can be modified if a different water chemistry for the seepage into the drift is determined to be more relevant; that is, one that accounts for changes due to interactions with the near field after waste emplacement.

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2. QUALITY ASSURANCE

The quality assurance (QA) program applies to the development of this report. The data provided in this report will be used for evaluating the post-closure performance of the monitored geologic repository (MGR) waste package and engineered barrier segment. The QAP-2-3 (*Classification of Permanent Items*) evaluation entitled *Classification of the Preliminary MGDS Repository Design* (CRWMS M&O 1998a, p. IV-11) has identified the waste package as a MGR (formerly MGDS) item important to safety and waste isolation. The waste package responsible manager has evaluated the technical document development activity in accordance with QAP-2-0, *Conduct of Activities*. The QAP-2-0 activity evaluation, *Commercial SNF WP Reference Designs* (CRWMS M&O 1999a), has determined that the preparation and review of this technical document is subject to *Quality Assurance Requirements and Description* (DOE 1998a) requirements. In accordance with AP-3.10Q, a work plan was developed, issued, and used in the preparation of this document (CRWMS M&O 1999b).

3. COMPUTER SOFTWARE AND MODEL USAGE

3.1 SOFTWARE APPROVED FOR QA WORK

None used.

3.2 SOFTWARE ROUTINES

Microsoft Excel 98 (Microsoft Office 98), loaded on a PowerMac G-3 with Mac OS 8.5.1. Calculations were performed electronically in this spreadsheet software package. The equations for which the calculations were performed are included in the text of the report. Electronic media containing the files of the calculations will be submitted as part of the records package.

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4. INPUTS

The following 3.10Q AMRs provide necessary inputs for the analyses of this 3.10Q AMR.

Physical and Chemical Environment Model AP-3.10Q; EB35; RPPM100A

Responsible Organization: PAO

Due Date: 2 Dec 99

Seepage/Invert Interactions AP-3.10Q; EB215; RPPM035A

Responsible Organization: PAO

Due Date: 30 Aug 99

Seepage/Backfill Interactions AP-3.10Q; EB165; RPPM015

Responsible Organization: PAO

Due Date: 10 Aug 99

Precipitates/Salts Analysis AP-3.10Q; EB45; RPPM105A;

Responsible Organization: PAO

Due Date: 7 Oct 99

In-Drift Gas Flux & Composition AP-3.10Q; EB175; RPPM055A;

Responsible Organization: PAO

Due Date: 4 Oct 99

Seepage/Cement AP-3.10Q; EB208; RPPM030A;

(has this been change to interaction w/ drift support materials A36 carbon steel)

Responsible Organization: PAO

Due Date: 18 Oct 99

Analysis of THC Processes/impacts on emplacement drift water chemistry/gas comp; N3010;
SPP7106;

Responsible Organization: NEPO

Due Date: 31 Aug 99

Description of base case results of NFE thermodynamic environment including THC and
THM; N3030; SL2000M4;

Responsible Organization: NEPO

Due Date: 02 Oct 99

Base case results of NFE for in-drift water chemistry/gas comp; N3040; SL20002M4;

Responsible Organization: NEPO

Due Date: 30 Sep 99

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The following 3.10Q report is not currently used in this 3.10Q report. However, if the information is relevant it will be incorporated in later versions.

Microbial Communities AP03.10Q; EB185; RPPM020A

Responsible Organization: PAO

Due Date: 14 Sep 99

4.1 PARAMETERS

4.1.1 Components of Atmospheric Air Exclusive of Water

The components of atmospheric air exclusive of water vapor is given in Table 4-1.

Table 4-1. Components of Atmospheric Air Exclusive of Water Vapor (Weast and Astle 1981)

Constituent	Content (%) by Volume	Content (ppm) by Volume
N ₂	78.084±0.004	
O ₂	20.946±0.002	
CO ₂	0.033±0.001	
Ar	0.934±0.001	
Ne		18.18±0.04
He		5.24±0.004
Kr		1.14±0.01
Xe		0.087±0.001
H ₂		0.5
CH ₄		2
N ₂ O		0.5±0.1

4.1.2 Water Vapor Pressure as a Function of Temperature

The water vapor pressure as a function of temperature is listed in Table 4-2. The data were taken from Weast and Astle (1981). The vapor pressure was given in Torr. The vapor pressure is also given in kPa by applying the conversion factor 760 torr = 101.32 kPa.

Table 4-2. Water Vapor Pressure as a Function of Temperature (Weast and Astle 1981)

Temp °C	kPa	torr*	Temp °C	kPa	torr*
0	0.61	4.59	155	543.38	4075.88
5	0.87	6.55	160	618.05	4636.00
10	1.23	9.21	165	700.73	5256.16
15	1.71	12.79	170	792.02	5940.92
20	2.34	17.54	175	892.43	6694.08
25	3.17	23.77	180	1002.56	7520.20
30	4.25	31.85	185	1123.03	8423.84
35	5.63	42.21	190	1254.95	9413.36
40	7.38	55.37	195	1398.32	10488.76
45	9.59	71.93	200	1554.35	11659.16
50	12.34	92.59	205	1722.90	12923.45
60	19.93	149.51	210	1906.20	14298.38

Temp °C	kPa	torr*	Temp °C	kPa	torr*
65	25.02	187.69	215	2104.20	15783.58
70	31.18	233.85	220	2317.80	17385.79
75	38.56	289.26	225	2547.90	19111.76
80	47.37	355.34	230	2795.10	20966.01
85	57.82	433.67	235	3060.40	22956.02
90	70.12	525.95	240	3344.70	25088.55
95	84.53	634.05	245	3648.80	27369.60
100	101.32	760.00	250	3973.60	29805.92
105	120.79	906.04	255	4320.20	32405.76
110	143.24	1074.44	260	4689.40	35175.13
115	169.02	1267.82	265	5082.30	38122.27
120	198.48	1488.80	270	5499.90	41254.68
125	232.01	1740.30	275	5943.10	44579.12
130	270.02	2025.42	280	6413.20	48105.33
135	312.93	2347.28	285	6911.10	51840.07
140	361.19	2709.28	290	7438.00	55792.34
145	415.51	3116.76	295	7995.20	59971.89
150	475.72	3568.37	300	8583.80	64386.97

4.1.3 Density of Water as a Function of Temperature

Table 4-3 lists the density (gm/liter) of water as a function of temperature. The data were taken from Perry and Chilton (1973).

Table 4-3. Density of Pure Water as a Function of Temperature (Perry and Chilton 1973)

Temp (°C)	Density (gm/liter)	Temp (°C)	Density (gm/liter)	Temp (°C)	Density (gm/liter)	Temp (°C)	Density (gm/liter)
0	0.99987	24	0.99733	48	0.98896	180	0.8866
1	0.99993	25	0.99708	49	0.98852	190	0.8750
2	0.99997	26	0.99682	50	0.98807	200	0.8628
3	0.99999	27	0.99655	51	0.98762	210	0.850
4	1.00000	28	0.99627	52	0.98715	220	0.837
5	0.99999	29	0.99598	53	0.98669	230	0.823
6	0.99997	30	0.99568	54	0.98621	240	0.809
7	0.99993	31	0.99537	55	0.98573	250	0.794
8	0.99988	32	0.99506	60	0.98324		
9	0.99981	33	0.99473	65	0.98059		
10	0.99973	34	0.99440	70	0.97781		
11	0.99963	35	0.99406	75	0.977489		
12	0.99952	36	0.99371	80	0.97183		
13	0.99940	37	0.99336	85	0.96865		
14	0.99927	38	0.99300	90	0.96534		
15	0.99913	39	0.99263	95	0.96192		
16	0.99897	40	0.99225	100	0.95838		
17	0.99880	41	0.99187	110	0.9510		
18	0.99862	42	0.99147	120	0.9434		
19	0.99843	43	0.99107	130	0.9352		

Temp (°C)	Density (gm/liter)	Temp (°C)	Density (gm/liter)	Temp (°C)	Density (gm/liter)	Temp (°C)	Density (gm/liter)
20	0.99823	44	0.99066	140	0.9264		
21	0.99802	45	0.99025	150	0.9173		
22	0.99780	46	0.98982	160	0.9075		
23	0.99757	47	0.98940	170	0.8973		

4.1.4 Surface Tension of Pure Water as a Function of Temperature

Table 4-4 lists the surface tension of pure water in contact with air (Weast and Astle 1981).

Table 4-4. Surface Tension of Pure Water as a Function of Temperature (Weast and Astle 1981)

Temperature (°C)	Surface Tension (dynes/cm)	Surface Tension (joules/m ²)	Surface Tension (dynes/cm)
20	72.75	0.07275	72.75
25	71.97	0.07197	71.97
30	71.18	0.07118	71.18
40	69.56	0.06956	69.56
50	67.91	0.06791	67.91
60	66.18	0.06618	66.18
70	64.40	0.06440	64.40
80	62.60	0.06260	62.60
100	58.90	0.05890	58.90

4.1.5 Atomic and Molecular Weights of Various Elements & Molecules

Table 4-5 is a list of the atomic weights of various elements and the molecular weights of various species (Weast and Astle 1981).

Table 4-5. Listing of the Atomic and Molecular Weights of Elements and Molecules Relevant to the Constituents in Yucca Mountain Waters

Element	Atomic weight (gm/gm-mol)	Molecule	Molecular Weight (gm/gm-mol)
H	1.0079	CaCO ₃	100.09
Na	22.98977	CaCl ₂	110.99
K	39.0983	Ca(OH) ₂	74.09
Mg	24.305	CaF ₂	78.08
Ca	40.08	CaSO ₄	136.14
C	12.011	Ca(NO ₃) ₂	164.09
Si	28.0855	H ₂ O	18.0153
N	14.0067	MgCO ₃	84.32
O	15.9994	MgCl ₂	95.22
S	32.06	MgF ₂	62.31
F	18.998403	Mg(NO ₃) ₂ • 2H ₂ O	184.35
Cl	35.435	MgSO ₄	120.37
		K ₂ CO ₃	138.21

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Element	Atomic weight (gm/gm-mol)	Molecule	Molecular Weight (gm/gm-mol)
		KHCO ₃	100.12
		KCl	74.56
		KF	58.10
		KNO ₃	101.11
		K ₂ SO ₄	174.27
		Na ₂ CO ₃	105.99
		NaHCO ₃	84.00
		NaCl	58.44
		NaF	41.99
		NaNO ₃	84.99
		Na ₂ SO ₄	142.04
		O ₂	31.9988

4.1.6 Equilibrium Constant for Water Dissociation, K_w

Table 4-6 lists the equilibrium constant for water dissociation, K_w , as a function of temperature (Weast and Astle 1981).

Table 4-6. Equilibrium Water Dissociation Constant as a Function of Temperature

Temperature (°C)	$-\log(K_w)$
0	14.9435
5	14.7338
10	14.5346
15	14.3463
20	14.1669
24	14.0000
25	13.9965
30	13.8330
35	13.6801
40	13.5348
45	13.3960
50	13.2617
55	13.1369
60	13.0171

4.1.7 Boiling Points of Saturated Solutions of Some Pure Salts

Table 4-7 lists the boiling points of several aqueous solutions of pure salts.

Table 4-7. Boiling Points of Aqueous Solutions of Pure Salts (Frazier 1928)

Salt	Boiling point (°C)
K ₂ SO ₄	102
KCl	108.6
NaCl	109
NaNO ₃	120.6

4.1.8 Equilibrium Relative Humidity of Selected Saturated Salt Solutions from 0 to 100°C

Table 4-8 lists the equilibrium relative humidities of selected saturated salt solutions (Greenspan 1977). These equilibrium relative humidities are also called the deliquescence points. The deliquescence points may also be described as the relative humidities at which these salts will begin sorbing water from the atmosphere.

4.1.9 Solubilities of Ca, Mg, Na, and K Salts/Minerals in Water

Table 4-9 is a list of solubilities of the salts/minerals of calcium, magnesium, sodium, and potassium (Weast and Astle 1981).

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Table 4-8. Equilibrium Relative Humidity of Saturated Aqueous Solutions of Various Pure Salts

Temp (°C)	KF	MgCl ₂	K ₂ CO ₃	MgNO ₃	NaNO ₃	NaCl	KCl	KNO ₃	NaOH	KOH	K ₂ SO ₄
0		33.66	43.13	60.35		75.51	88.61	96.33			98.77
5		33.60	43.13	58.86	78.57	75.65	87.67	96.27		14.34	98.48
10		33.47	43.14	57.36	77.53	75.67	86.77	95.96		12.34	98.18
15		33.30	43.15	55.87	76.46	75.61	85.92	95.41	9.57	10.68	97.89
20		33.07	43.15	54.38	75.36	75.47	85.11	94.62	8.91	9.32	97.59
25	30.85	32.78	43.16	52.89	74.25	75.29	84.34	93.58	8.24	8.23	97.30
30	27.27	32.44	43.17	51.40	73.14	75.09	83.62	92.31	7.58	7.38	97.00
35	24.59	32.05		49.91	72.06	74.87	82.95	90.19	6.92	6.73	96.71
40	22.68	31.60		48.42	71.00	74.68	82.32	89.03	6.26	6.26	96.41
45	21.46	31.10		46.93	69.99	74.52	81.74	87.03	5.60	5.94	96.12
50	20.80	30.54		45.44	69.04	74.43	81.20	84.78	4.94	5.72	95.82
55	20.60	29.93			68.15	74.41	80.7		4.27	5.58	
60	20.77	29.26			67.35	74.50	80.25		3.61	5.49	
65	21.18	28.54			66.64	74.71	79.85		2.95	5.41	
70	21.74	27.77			66.04	75.06	79.49		2.29	5.32	
75	22.33	26.94			65.56	75.58	79.17		1.63		
80	22.85	26.05			65.22	76.29	78.90				
85	23.20	25.11			65.03		78.68				
90	23.27	24.12			65.00		78.50				
95		23.07									
100		21.97									

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Table 4-9. Solubilities of Ca, Mg, Na, and K Salts/Minerals in Water

Compound	Formula		Low Temperature			High Temperature		
			Temp (°C)	Solubility gms/100cc	Solubility mg/liter*	Temp (°C)	Solubility gms/100cc	Solubility mg/liter*
Calcium sulfate	CaSO ₄	Natural anhydrite	30	0.2090	2090		0.1619	1619
Calcium sulfate dihydrate	CaSO ₄ • 2H ₂ O	Natural gypsum		0.2410	2410		0.222	2220
Calcium nitrate	Ca(NO ₃) ₂		18	121.2	1212000		376	3760000
Calcium chloride	CaCl ₂		20	74.5	745000		159	1590000
Calcium fluoride	CaF ₂	Natural fluorite	18	0.0016	16		0.0017	17
Calcium carbonate	CaCO ₃	Calcite	25	0.0014	14		0.0018	18
Calcium hydroxide	Ca(OH) ₂		0	0.1850	1850		0.077	770
Sodium Sulfate	Na ₂ SO ₄	Natural thenardite	0	4.760	47600		42.7	427000
Sodium nitrate	NaNO ₃	Soda niter	25	92.1	921000		180	1800000
Sodium chloride	NaCl	Halite	0	35.7	357000		39.12	391200
Sodium fluoride	NaF	Natural villiaumite	18	4.22	42200			0
Sodium carbonate	Na ₂ CO ₃		0	7.1	71000		45.5	455000
Sodium bicarbonate	NaHCO ₃		0	6.9	69000		16.4	164000
Sodium hydroxide	NaOH		0	42.0	420000		347	3470000
Sodium silicate	Na ₂ SiO ₃	Metasilicate		Soluble			Dissolves	
Magnesium sulfate	MgSO ₄		0	26	260000		73.8	738000
Magnesium nitrate	Mg(NO ₃) ₂			124	1240000		Vs	
Magnesium chloride	MgCl ₂		20	54.25	542500		72.7	727000
Magnesium fluoride	MgF ₂	Natural sellaite	18	0.0076	76		Insoluble	
Magnesium carbonate	MgCO ₃	Natural magnesite		0.0106	106			
Magnesium carbonate trihydrate	MgCO ₃ • 3H ₂ O	Natural hydromag		0.04	400		0.011	110
Magnesium carbonate basic	3MgCO ₃ • Mg(OH) ₂	Natural nesqueho	16	0.179	1790		Dissolves	
Magnesium hydroxide	Mg(OH) ₂	Natural brucite	18	0.0009	9		0.004	40

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Compound	Formula		Low Temperature			High Temperature		
			Temp (°C)	Solubility gms/100cc	Solubility mg/liter*	Temp (°C)	Solubility gms/100cc	Solubility mg/liter*
Potassium sulfate	K ₂ SO ₄	Arcanite	25	12	120000		24.1	241000
Potassium sulfate, hydrogen	KHSO ₄	Mercallite	0	36.3	363000		121.6	1216000
Potassium nitrate	KNO ₃	Saltpeter	0	13.3	133000		247	2470000
Potassium chloride	KCl	Sylvite	20	23.8	238000		56.7	567000
Potassium fluoride	KF		18	92.3	923000		Very soluble	
Potassium carbonate	K ₂ CO ₃		20	112	1120000		156	1560000
Potassium carbonate, hydrogen	KHCO ₃			22.4	224000		60	600000
Potassium hydroxide	KOH		15				178	1780000

4.1.10 Decomposition/Melting Temperatures of Some Bicarbonate/Carbonate Species

Table 4-10 is list of the decomposition/melting temperatures of relevant bicarbonate/carbonate species (Weast and Astle 1981).

Table 4-10. Decomposition/Melting Temperatures of Relevant Bicarbonate/Carbonate Species

Species	Decomposition Temp (°C)	Melting Temp (°C)	Decomposition Product
KHCO ₃	100	N/A	CO, CO ₂ , KOH, K ₂ O
NaHCO ₃	250	N/A	CO ₂ , NaOH

4.1.11 Adsorbed Water Films as a Function of Relative Humidity and Temperature

Figures 4-1 and 4-2 show the amount of water adsorbed on a nickel as a function of temperature (20 to 80°C) and relative humidity (20 to 98% RH) (Lee and Staehle 1997).

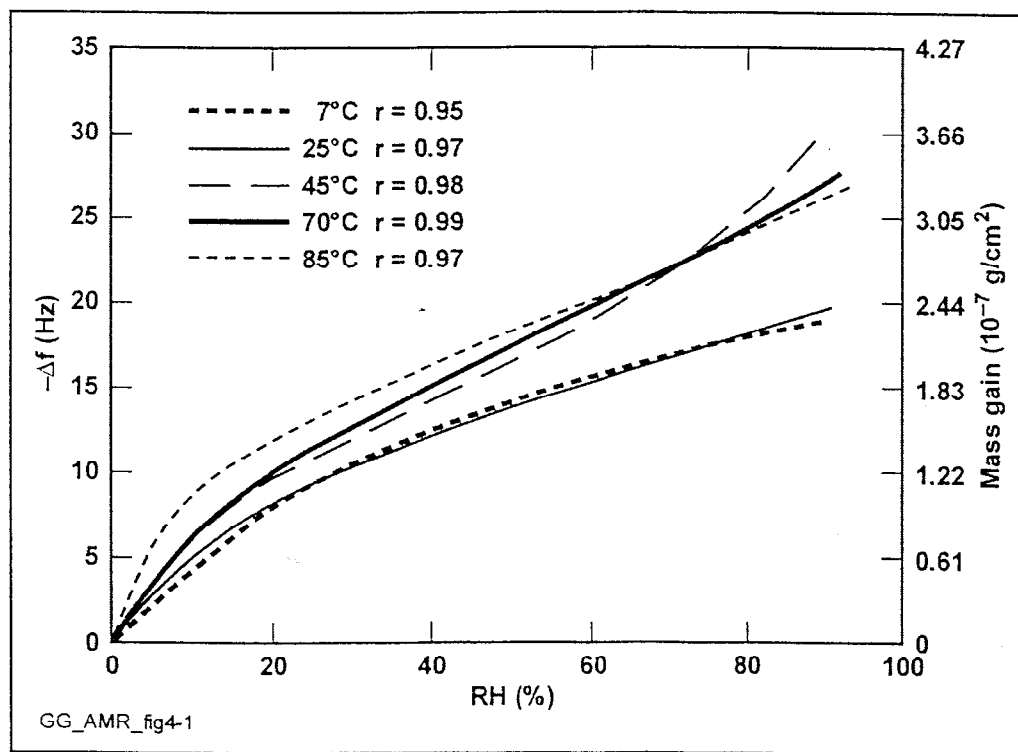


Figure 4-1. Amount of Water Adsorbed on a Nickel as a Function of Temperature (20 to 80°C) (Lee and Staehle 1997)

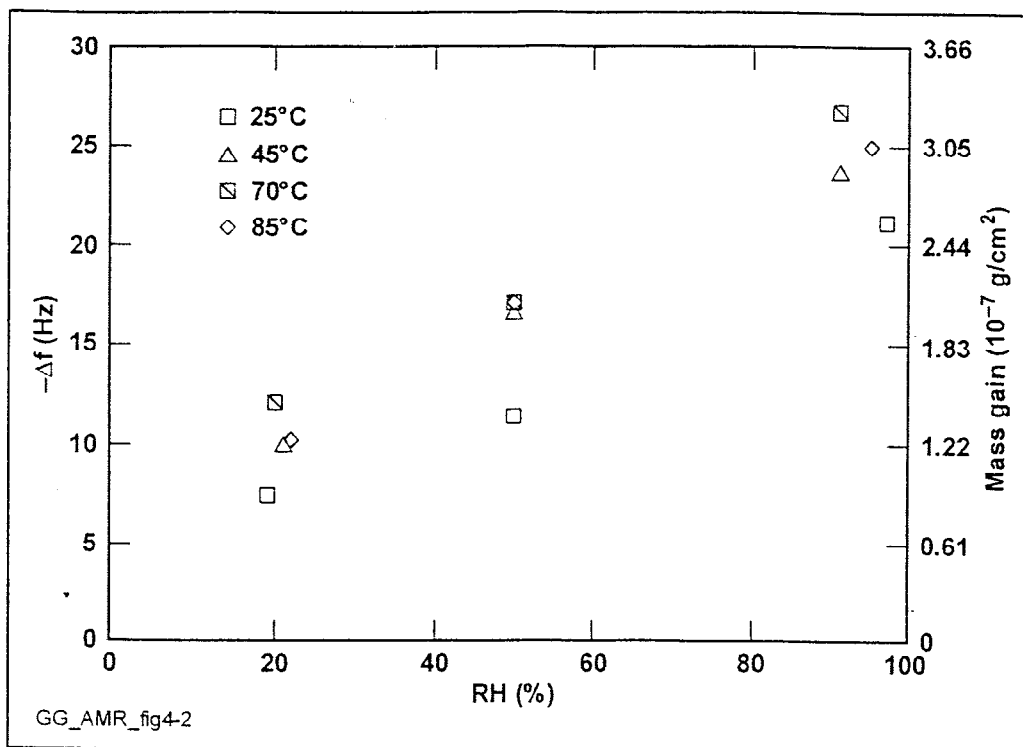


Figure 4-2. Amount of Water Adsorbed on a Nickel as a Function of Relative Humidity (20 to 98% RH) (Lee and Staehle 1997)

4.1.12 Vapor Pressure Lowering of Aqueous NaCl Solutions

Table 4-11 shows the water vapor pressure lowering of aqueous solutions by NaCl solutions at temperatures from 20 to 100°C (Frazier 1928). The experimental data were reported in terms of two parameters, m and $100R$, where

m molality (gram-formula weights (moles) of solute per 1000g H₂O)

and

$$100R = 100(P^0 - P)/mP^0.$$

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Table 4-11. Experimental Data on the Vapor Pressure Lowering of Aqueous NaCl Solutions as a Function of Temperature (Frazier 1928)

20-25°C		80°C		100°C	
M	100R	M	100R	M	100R
0.1	3.29	4.0	3.65	2.5	3.47
0.2	3.28	5.0	3.79	3.5	3.57
0.4	3.27	6.0	3.91	4.0	3.62
0.6	3.27			5.0	3.76
0.8	3.28			6.3	3.91
1.0	3.30			6.7	3.89
2.0	3.42				
2.8	3.53				
5.0	3.87				
6.0	3.99				

From the vapor pressure lowering data of aqueous NaCl solutions (see Table 4-12), the relative humidity (*RH*) as a function of concentration (both molality and ppm) is calculated.

$$100R = 100(P^0 - P)/mP^0$$

where

P^0 vapor pressure of pure solvent (water)

P partial vapor pressure of the solvent (water) from the solution.

Rearranging the above equation in terms of P gives

$$P = P^0 - m \times P^0 \times (100R/100).$$

The relative humidity (*RH*) is calculated by the following equation:

$$RH = P/P^0.$$

From the molality data the concentration in terms of ppm is calculated from the following equation:

$$C(ppm) = m \times MW / (1000g_{H_2O} + m \times MW)$$

where

MW = molecular weight of solute = (55.44gm/mole of NaCl).

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Table 4-12. NaCl Molality as a Function of Temperature

Temperature (°C)	M (molality)	100R	Concentration (ppm)	P (kPa)	RH (%)
20–25	0.1	3.29	5810	3.16	99.7
(P ⁰ =3.17 kPa)	0.2	3.28	11553	3.15	99.3
	0.4	3.27	22842	3.13	98.7
	0.6	3.27	33876	3.10	98.0
	0.8	3.28	44664	3.08	97.4
	1.0	3.30	55213	3.06	96.7
	2.0	3.42	104649	2.95	93.2
	2.8	3.53	140622	2.85	90.1
	5.0	3.87	226126	2.55	80.7
	6.0	3.99	259610	2.41	76.1
80					
(P ⁰ =47.34 kPa)	4.0	3.65	189470	40.43	85.4
	5.0	3.79	226126	38.37	81.1
	6.0	3.91	259610	36.23	76.5
100					
P ⁰ =101.32 kPa	2.5	3.47	127476	92.53	91.3
	3.5	3.57	169808	88.66	87.5
	4.0	3.62	189470	86.65	85.5
	5.0	3.76	226126	82.27	81.2
	6.3	3.91	269098	76.36	75.4
	6.7	3.89	281376	74.91	73.9

4.1.13 Composition of Well J13 Water

Table 4-13 lists the composition of well J13 water (Harrar 1990).

Table 4-13. Composition of Well J13 Water (Harrar 1990)

Species	Concentration (mg/l)
Na	45.80
Si	28.5
Ca	13.0
K	5.04
Mg	2.01
F	2.18
Cl	7.14
NO ₃	8.78
SO ₄	18.4
HCO ₃	128.9
pH	7.41

4.1.14 Composition of Waters from Field Studies (TBD)

The composition of waters that have been obtained from the Single Heater Test and the Drift Scale Test field studies at Yucca Mountain will be noted in this section.

4.1.15 Compositions of Perched and Pore Waters from Yucca Mountain (TBD)

The compositions of waters that have been obtained from perched and pore waters from Yucca Mountain will be noted in this section.

4.1.16 Compositions of Waters Contacting the Drip Shield and Waste Package Outer Barrier Surfaces (TBD)

When the analyses from N3080 "Description Abstract NFE In-Drift Water," EB225 "In-Drift THC Analysis," EB45 "Precipitate Salts Analysis," and possibly EB165 "Seepage/Backfill Interaction" have been completed, the results will be analyzed in the context of this 3.10Q AMR.

4.1.17 Henry's Law Constants for the Solubility of Oxygen in Several Aqueous Solutions

Table 4-14 lists parameters for calculating the Henry's Law Constant for oxygen solubility in pure water and three aqueous NaCl solutions (Cramer 1980). The Henry's Law constant, k , was determined experimentally, and the variation with temperature fit to the following equation.

$$\ln k = a_0 + a_1/T + a_2/T^2 + a_3/T^3 + a_4/T^4$$

where a_0, a_1, a_3 , and a_4 , are experimentally determined constants, and T is temperature in Kelvin.

Also included in Table 4-14 are the characteristics of the fluids for which the k values were determined.

Table 4-14. Coefficients for Henry's Law Constants for the Oxygen Solubility in the NaCl Solutions and Demineralized Water

Solution	Molality (moles/ 1,000g)	Molarity (moles/ liter)	Coefficients					Std dev, %
			a_0	$a_1(10^4)$	$a_2(10^7)$	$a_3(10^9)$	$a_4(10^{11})$	
Demineralized water	0	0	-35.4408	5.58970	-2.67211	5.80947	-4.91667	5.6
NaCl-1	0.87	0.85	-23.8312	4.05434	-1.89188	4.02544	-3.35511	4.5
NaCl-2	2.97	2.78	-14.7705	2.95905	-1.38197	2.97589	-2.51663	5.3
NaCl-3	5.69	5.09	18.7594	-2.02638	1.38823	-3.75034	3.52602	4.9

Table 4-15 lists the Henry's Law constant that was calculated using the coefficients in Table 4-14.

$$\ln k = a_0 + a_1/T + a_2/T^2 + a_3/T^3 + a_4/T^4$$

Table 4-15. Calculated Henry's Law Constants for Oxygen Solubility in Three Aqueous Solutions

Temp (°C)	Henry's Law Constants, <i>k</i> MPa			
	Demineralized Water	NaCl-1	NaCl-2	NaCl-3
0	2427.81	3948.40	9404.30	21073.80
5	2863.54	4464.37	10208.99	21453.07
10	3297.81	4963.39	10938.31	21966.03
15	3722.91	5440.21	11591.48	22565.62
20	4132.95	5891.19	12170.10	23213.24
25	4523.66	6313.95	12677.33	23876.50
30	4892.07	6707.11	13117.18	24528.06
35	5236.23	7069.92	13494.07	25144.91
40	5554.97	7402.14	13812.51	25708.11
45	5847.63	7703.84	14076.89	26202.50
50	6113.91	7975.28	14291.32	26616.56
55	6353.75	8216.84	14459.60	26942.21
60	6567.23	8428.99	14585.22	27174.52
65	6754.52	8612.21	14671.31	27311.44
70	6915.85	8767.04	14720.70	27353.44
75	7051.50	8894.05	14735.98	27303.16
80	7161.78	8993.82	14719.45	27165.00
85	7247.07	9067.00	14673.26	26944.75
90	7307.78	9114.26	14599.38	26649.23
95	7344.41	9136.37	14499.63	26285.95
100	7357.55	9134.14	14375.74	25862.82
105	7347.86	9108.45	14229.36	25387.88
110	7316.12	9060.26	14062.06	24869.08
115	7263.18	8990.61	13875.36	24314.14
120	7190.02	8900.61	13670.75	23730.39
125	7097.72	8791.44	13449.69	23124.66
130	6987.44	8664.34	13213.58	22503.24
135	6860.44	8520.59	12963.64	21871.86
140	6718.03	8361.53	12701.82	21235.62

4.1.18 Evaporative/Boiling Concentrating of a Simulated Well J13 Water Near the Boiling Point of the Concentrated Water (DTN #LL990703005924.083 and TBD#)

Table 4-16 lists the composition of waters that result from the evaporative/boiling concentrating of simulated concentrated well J13 water. The initial waters are nominally 100 times the concentration of well J13 waters. Samples were measured after concentrating 1 liter, 2 liters, etc. of solution to approximately 100 to 200 ml. The water was dripped onto and drained through

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heated crushed tuff. Heat was supplied to the system in order to keep the temperature of the water at or near its boiling point.

The testing is continuing in order to obtain the compositions of aqueous solutions that result from progressively more evaporative concentrating, and also to obtain the boiling point and pH of the resulting aqueous solutions.

Table 4-16. The Compositions of Evaporatively Concentrated Simulated 100x Well J13 Water

Species	Starting Sol'n (mg/liter)	Solution Compositions (mg/liter)						
		Amount of Initial Solution Concentrated to 100–200 ml and the Estimated Boiling Point (°C)						
		1	2	3	4	5	6	7
Sample #	Initial J13 Batch 3	ECBP 042399-0	ECBP 050699-0	ECBP 051899-0	ECBP 060199-0	ECBP 061099-0	ECBP 061499-0	ECBP 061599-0
DTN #LL990703005924.083								
Boiling Point		101					108	
Ca	6	735	0	0	48	0	62	587
K	535	3885	7985	15878	21180	24510	21532	8389
Mg	0	0	0	0	0	0	0	0
Na	4360	43317	106465	177301	202726	226721	190711	92279
Si	13	7461	30875	79388	118912	121020	90741	42504
F	210	2230	4392	4393	0	843	0	3020
Cl	729	7446	16130	32814	38125	49021	49831	15715
NO ₃	846	9370	14905	34402	40243	51165	50443	15184
SO ₄	1790	19326	38594	53455	41150	48408	32913	30480
HCO ₃	9556	28921	51776	107033	98361	89496	79006	37750

4.1.19 Evaporative/Boiling Concentrating of Waters from Field Studies Near the Boiling Point of the Concentrated Water (TBD#)

This section will document the compositions, boiling points, and pH of aqueous solutions that result from the evaporative concentrating of simulated field studies waters, including those from the Single Heater Test and the Drift Scale Test at Yucca Mountain. This analysis will be performed to determine if significant differences exist between the characteristics of these waters and those of simulated well J13 water.

4.1.20 Evaporative Concentrating of Simulated J13 at Temperatures Below the Boiling Point (DTN #LL990703005924.083 and TBD#)

Table 4-17 characterizes the aqueous solutions that may be in contact with the DSs and the WPOBs in the temperature range in which susceptibility to aqueous electrochemical corrosion is possible. This range includes temperatures between 85 and 110°C, and relative humidities from 50 to 90%. Tests are now underway to determine the composition and pH of the aqueous solutions that result from the evaporative concentrating of simulated J13 water in these ranges.

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Table 4-17. Results of the Evaporative Concentration of a Simulated Well J13 Water Under Conditions of Constant Temperature and Relative Humidity

Species	Starting Sol'n (mg/liter)	Final Sol'n 85%RH/90°C (mg/liter)
Sample #	Initial J13 Batch 1	J13-01
DTN #LL990703005924.083		
Cl	730	15200
NO ₃	732	14600
SO ₄	1633	30400
F	208	3500
HCO ₃ [*]		11370
Na	4210	79700
K	517	10020
Ca	5.48	26
Mg	2.04	0

*Total inorganic carbon expressed as bicarbonate.

4.1.21 Evaporative Concentrating of Waters from Field Studies at Temperatures Below the Boiling Point (TBD)

This section will document the compositions, boiling points, and pH of aqueous solutions that result from the evaporative concentrating of simulated field studies waters, including those from the Single Heater Test and the Drift Scale Test at Yucca Mountain. This analysis will be performed to determine if significant differences exist between the characteristics of these waters and those of simulated well J13 water.

4.1.22 Gas Phase Compositions in Drift (TBD)

The composition of the gas phase has a controlling influence on the water chemistry of thin films. Important parameters include the partial pressure of water vapor (H₂O), oxygen (O₂), and carbon dioxide (CO₂). The water chemistry can also be affected by the presence of aerosols and dust particles containing soluble salts. Aerosols and dust particles in the atmosphere can contain chlorides, sulfates, and nitrates. Because aerosols and dust particles contain soluble salts they can effect water chemistry if present in sufficient quantities.

For the analyses performed in this 3.10Q, the analysis of the gas phase composition is initially unnecessary. The analyses are performed as a function of water vapor content and temperature.

It is not known if the mechanisms for aerosol formation or dry deposition of dust particles will be operative in the drifts after the waste packages (WPs) have been emplaced. Active ventilation may be a mechanism for depositing salts on the DSs and WPs. Further, the soluble salt content of the "dust" in the drifts has not been characterized.

4.2 CRITERIA

The applicable requirements reproduced below are from Section 1.2, "System Design Criteria" of *Uncanistered Spent Nuclear Fuel Disposal Container System Description Document* (CRWMS 1999). For the sake of clarity, the original section numbers appear in parentheses after the text.

4.2.1 "System Environment Criteria" (Section 1.2.3)

"The disposal container shall meet all performance requirements during and after exposure to the emplacement drift external environments identified in Table 1-8. (TBD-234)." (Section 1.2.3.1)

Table 4-18. Emplacement Drift External Environment (Table 1-8)

Environment	Range	Duration/Frequency of Occurrence
TBD	TBD	TBD

The analyses contained in this AMR characterize the range of environments possible on the surfaces of the DSs and WPOBs as a function of the in-drift environment in order that testing may be conducted to determine if the performance requirements for the WPs and DS will be met.

4.2.2 "System Performance Criteria" (Section 1.2.1)

"The disposal container shall be designed such that no more than 1 percent of all waste packages breach during the first 1,000 years after emplacement (breaching is defined as an opening through the wall of the waste package through which advective or diffusive transport of gas or radionuclides can occur)." (Section 1.2.1.1)

"The disposal container shall be designed such that for 10,000 years after permanent closure of the repository the release rate of any radionuclide from all waste packages shall not exceed one part in 100,000 per year of the inventory of that radionuclide calculated to be present at 1,000 years following permanent closure; provided, that this requirement does not apply to any radionuclide which is released at a rate less than 0.1 percent of the calculated total release rate limit. The calculated total release rate limit shall be taken to be one part in 100,000 per year of the inventory of radioactive waste, originally emplaced in the underground facility, that remains after 1,000 years of radioactive decay." (Section 1.2.1.4)

The analyses contained in this AMR characterize the range of environments possible on the surfaces of the DSs and WPOBs. The environments' conditions will be considered in evaluating the performance of the candidate materials for the DSs and WPOBs to determine if the performance requirements for the WPs and DS listed above will be met.

4.3 CODES AND STANDARDS

No codes or standards are currently used in this document.

5. ASSUMPTIONS

The following assumptions were used in Section 6 of this report. The assumptions concern the nature of the water contacting the surfaces of the DSs and the WPOBs, and the expected DS and WPOB temperature and relative humidity histories.

- The composition of well J13 water is representative of water that will contact the DSs' and WPOBs' surfaces. (TBV)

Information concerning this assumption will be obtained from other 3.10Q AMRs, such as "N3080 Description Abstract NFE In-Drift Water." If another water chemistry is determined to be more appropriate, then sensitivity analyses will be performed to determine the consequences of the different water chemistries.

- The temperatures of the DSs and WPOBs are less than 300°C. (TBV)

Information concerning this assumption will be obtained from other 3.10Q AMRs, such as "EB225 In-Drift THC Analysis."

- The total pressure in the drifts is limited to the ambient nominal atmospheric pressure (87.67 kPa), which corresponds to a pure-water boiling point of 96°C. (TBV)

Information concerning this assumption will be obtained from other 3.10Q AMRs, such as "EB175 Gas Flux & Composition."

- The gas phase composition of the drift air exclusive of water is either the same as "atmospheric air" or has a concentration of CO₂ that is a factor of three higher. (TBV)

Information concerning this assumption will be obtained from other 3.10Q AMRs, such as "EB175 Gas Flux & Composition."

6. ANALYSIS

6.1 INTRODUCTION

The environments on the drip shield and waste package outer barrier are controlled by the compositions of the waters that contact these components, the temperature (T) of these components, and the effective relative humidity (RH) at these components. Because the composition of the waters that are expected to enter the emplacement drifts (either by seepage flow or by episodic flow) have not been specified, well J13 water was chosen as the reference water (Harrar 1990).

Section 6.2 discusses the accessible RH for the temperatures of interest at the repository horizon. Section 6.3 discusses the adsorption of water on metal alloys in the absence of hygroscopic salts.

Because the temperatures of the DSs and the WPOBs are higher than those of the surrounding near-field environment, the relative humidity at the DSs and the WPOBs will be lower than that of the surrounding near-field environment. This difference is a result of the water partial pressure in the drift being constant and no higher than the equilibrium water vapor pressure at the temperature of the drift wall. Hence,

$$P_{H_2O}(WP) = P_{H_2O}(DW), \text{ but}$$

$$P_{H_2O}^0(WP) > P_{H_2O}^0(DW) \text{ because } T(WP) > T(DW), \text{ and therefore,}$$

$$RH(WP) < RH(DW), \text{ with } RH = P_{H_2O}/P_{H_2O}^0,$$

where

P_{H_2O} is the partial pressure of water,

$P_{H_2O}^0$ is the equilibrium vapor pressure of water,

and WP and DW indicate the waste package and drift wall, respectively.

Consequently, some of the water that contacts the DSs or WPOBs will necessarily evaporate in order for the remaining aqueous solutions to equilibrate with the local relative humidity. To understand the following sections, it is important first to understand the effect of concentrating the ionic species in the water, that is, which ions will remain in solution and which ions will form precipitates.

The deliquescence points define the lower RH limit for which aqueous salt solutions will exist. The deliquescence points are the RH s at which hygroscopic salts will sorb water from the atmosphere and form their most concentrated aqueous salt solutions. At higher values of RH , the aqueous solutions become more dilute. When these salt solutions are in contact with metals or alloys, electrochemical corrosion processes are enabled. Hence, it is the deliquescence point for a

particular salt or salt mixture which defines the condition necessary for aqueous electrochemical corrosion at a particular temperature.

In Section 6.4, a discussion of the types of salt/mineral scale that can form on "heat transfer surfaces" is presented.

6.2 THE EH AND PH OF AQUEOUS SOLUTIONS UNDER RELEVANT REPOSITORY CONDITIONS

6.2.1 Accessible Relative Humidity Conditions

At the elevation of the potential repository the nominal atmospheric pressure is 87.67 kPa; this corresponds to a boiling point of 96°C for pure water. Figure 6-1 shows the relative humidities that are accessible as a function of temperature for the fixed total pressure of 87.67 kPa. For comparison, the maximum relative humidity values are also plotted for a fixed total pressure of 101.32 kPa, with the corresponding boiling point of water equal to 100°C.

The consequence of the fixed total system pressure is that the relative humidities decrease for temperatures above the boiling point of water, as shown in Figure 6-1.

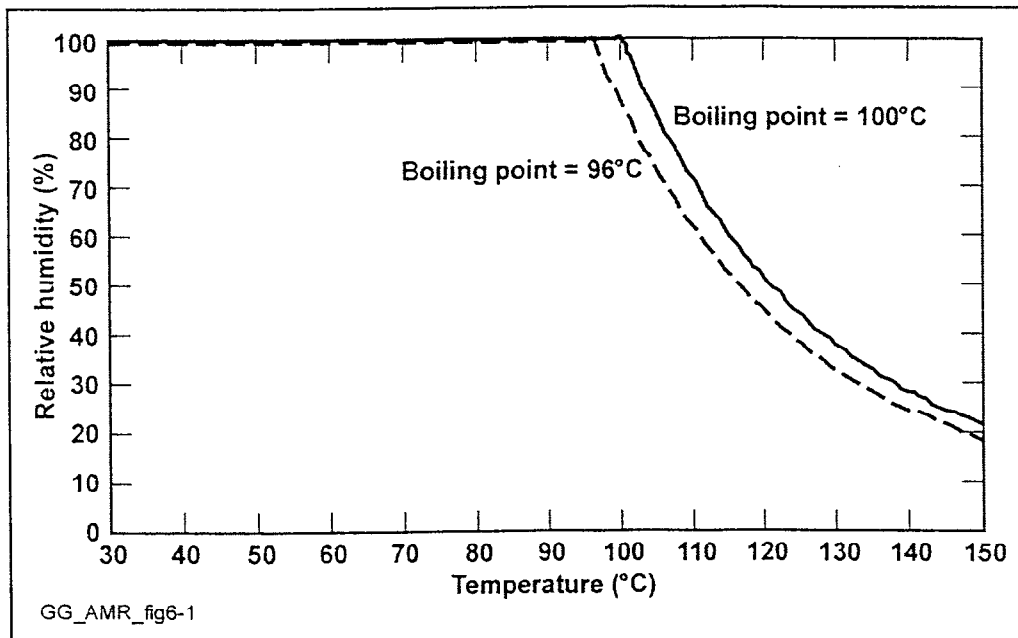


Figure 6-1. Maximum Relative Humidity versus Temperature for Boiling Points of 96°C and 100°C

6.2.2 Gas Phase Composition as a Function of Relative Humidity

The following tables and accompanying figures show the variation of oxygen (O₂) and carbon dioxide (CO₂) content of the drift air as a function of temperature and relative humidity. Also included in the table is the water vapor pressure as a function of temperature (Weast and Astle

1981). Water (P_{H_2O}), carbon dioxide (P_{CO_2}) and oxygen (P_{O_2}) partial pressure were calculated according to the following:

$$P_{H_2O} = x_{RH} \times P_{H_2O}^0,$$

$$P_{CO_2} = x_{CO_2} \times (P_{total} - x_{RH} \times P_{H_2O}^0), \text{ and}$$

$$P_{O_2} = x_{O_2} \times (P_{total} - x_{RH} \times P_{H_2O}^0)$$

where

x_{CO_2} carbon dioxide volume fraction of air

x_{O_2} oxygen volume fraction of air

P_{total} total atmospheric pressure

x_{RH} fractional relative humidity

$P_{H_2O}^0$ water vapor pressure.

Figures 6-2 and 6-3 are plots of the calculations for the oxygen and carbon dioxide partial pressures for two scenarios. One case assumes that the partial pressure of water is always equal to its vapor pressure. The other scenario assumes that $RH = 90\%$ for $T \leq 100^\circ\text{C}$ and $P_{H_2O} = 0.90 \times P_{total}$ for $T > 100^\circ\text{C}$.

6.2.3 Oxygen Solubility

The electrochemical potential of an aqueous solution is a determinant of the corrosion processes that can occur on a metal surface. Dissolved oxygen strongly influences the electrochemical potential of the aqueous solution. Oxygen solubility in pure water and various salt solutions (in particular, NaCl) have been studied by Cramer (1980).

The mole fraction, x_{O_2} of molecular oxygen in the aqueous solution with some simplifying assumption was given by:

$$x_{O_2} = P_{O_2}/k$$

where P_{O_2} is the partial pressure of oxygen in the gas phase and k is the Henry's Law constant. An analytical expression for k was given as follows:

$$\ln k = a_0 + a_1/T + a_2/T^2 + a_3/T^3 + a_4/T^4$$

where k is in MPa and T in K. The constants a_0 , a_1 , a_2 , a_3 , and a_4 are given in Table 4-14.

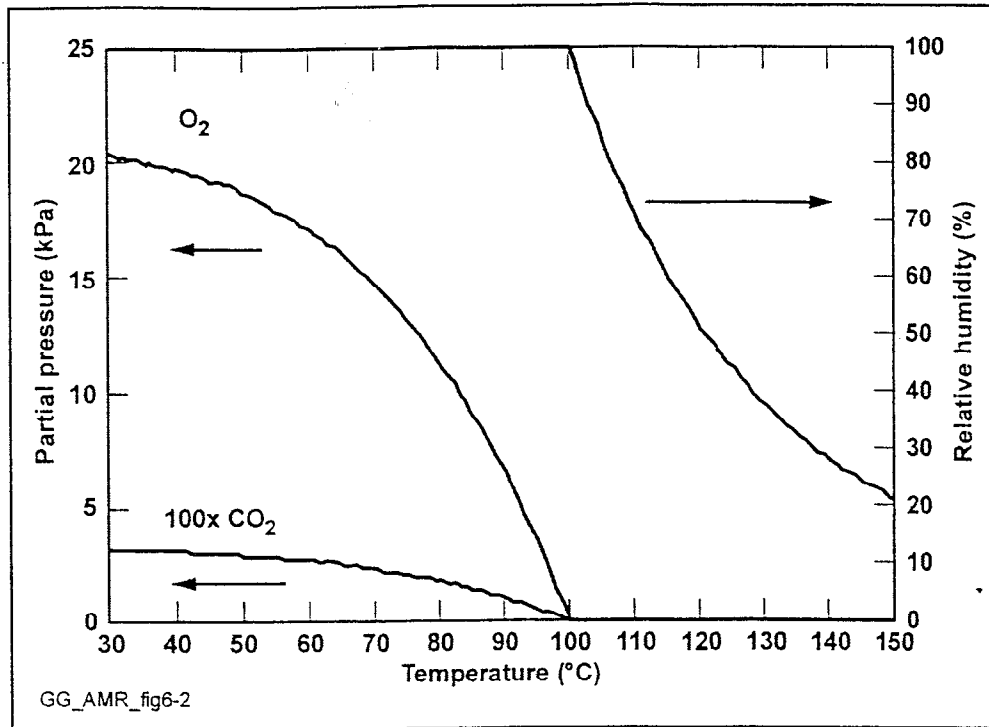


Figure 6-2. Calculated Partial Pressure of O₂ and CO₂ Assuming H₂O Partial Pressure is at its Maximum; That is, 100% RH for $T \leq 100^\circ\text{C}$ and 101.32 kPa for $T > 100^\circ\text{C}$

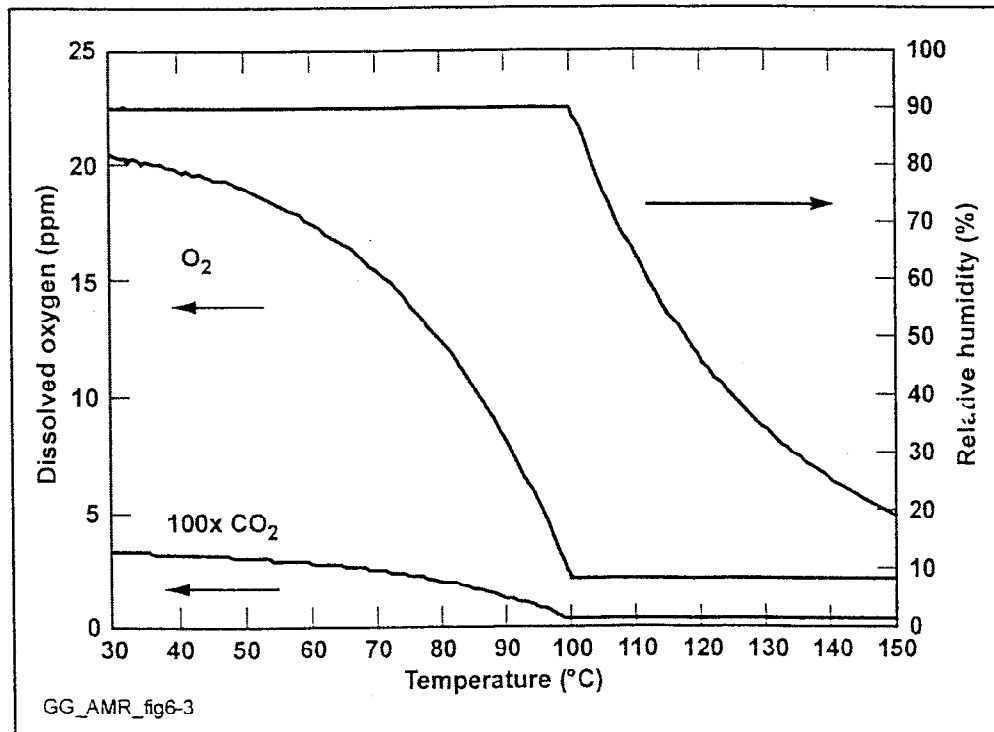


Figure 6-3. Calculations of O₂ and CO₂ Partial Pressures Assuming RH = 90% for $T < 100^\circ\text{C}$ and the Partial Pressure of Water is Equal to 0.9 Times the Total System Pressure Above 100°C

The solubility of oxygen in parts per million (ppm) by weight is given by:

$$D_{O_2}(\text{ppm}) = (P_{O_2}/k) \times (1000/MW_{H_2O} + M_{\text{solute}}) \times MW_{O_2}/\rho_{\text{soln}}$$

where

1000 weight one liter of the solvent in grams

MW_{H_2O} molecular weight of water (18.0153 gm/gm-mol)

MW_{O_2} molecular weight of O_2

M_{solute} molarity of the solute and

ρ_{soln} density of the solution in gm/liter.

The density of the fluid is given by

$$\rho_{\text{soln}} = \rho_{H_2O} + (0.03378 + 0.5622 \times 10^{-5} \times \exp(T/66.0)) \times \rho_{H_2O} \times m_{\text{soln}}$$

where

ρ_{H_2O} density of water

m_{soln} molality of solutions.

Plotted in Figures 6-4 and 6-5 are the solubilities of oxygen in three aqueous solutions for two cases of different partial pressures of oxygen with a fixed total pressure. In Figure 6-4, the partial pressure of H_2O is assumed to be at its maximum value, i.e., 100% RH below 100°C and 101.32 kPa above 100°C. Above 100°C there is no partial pressure of oxygen—therefore no oxygen is in any of the solutions. Below 100°C the partial pressure of oxygen is steadily increasing with decreasing temperature (see Figure 6-2) and hence the oxygen solution concentrations are increasing. Evident in Figure 6-2 is the “salting out” effect; that is, the solutes in solution cause a decrease in the oxygen solubility for a given partial pressure of oxygen. It worth noting that the salt solutions are *not* in equilibrium with the water vapor pressure under these conditions. Under the condition of 100% RH, waters in equilibrium with the surrounding gas phase are infinitely dilute. Therefore, both aqueous salt solutions would tend to become more dilute over time. The equilibrium concentration dependence on RH is discussed in Section 6.3.1.

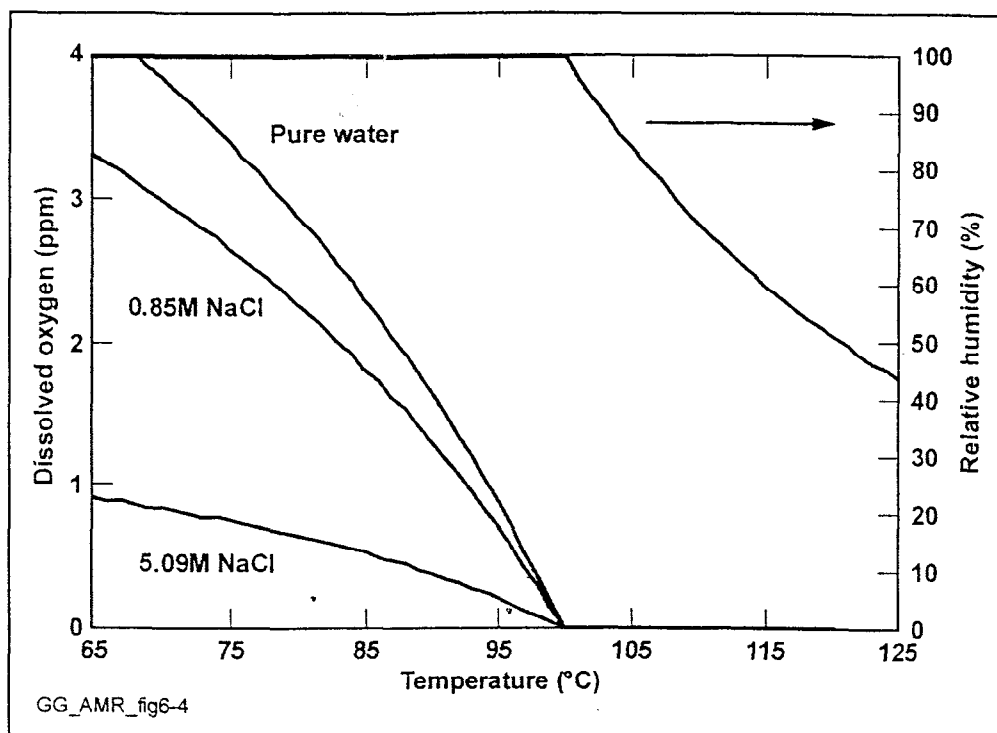


Figure 6-4. Dissolved Oxygen Concentration (ppm) for Three Aqueous Solutions. Water Partial Pressure: 100% RH for $T \leq 100^\circ\text{C}$ and 101.32 kPa for $T > 100^\circ\text{C}$

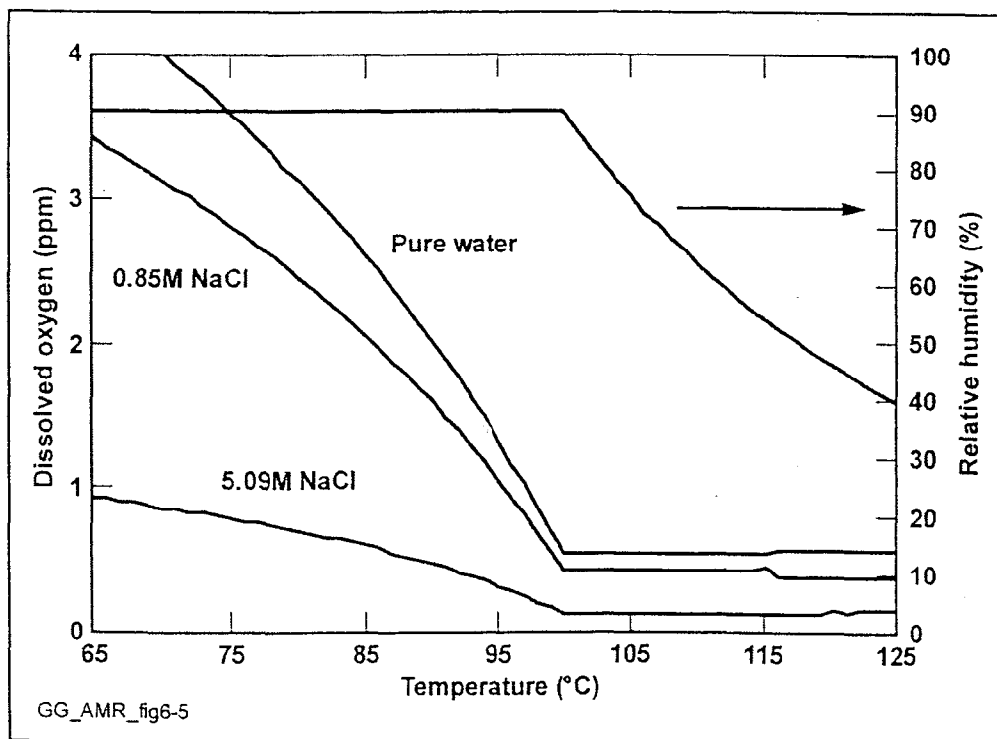


Figure 6-5. Dissolved Oxygen Concentration (ppm) for Three Aqueous Solutions. Partial Pressure of Water Determined by: 90% RH for $T \leq 100^\circ\text{C}$ and 87.67 for $T > 100^\circ\text{C}$

In Figure 6-5 the dissolved oxygen content is calculated for the three aqueous solutions assuming that the water partial pressure is determined by the following conditions: 90% RH for $T \leq 100^\circ\text{C}$ and 87.67 kPa for $T > 100^\circ\text{C}$. For all the solutions, a significant dissolved oxygen concentration is evident above 100°C . As in the previous example, for at least a portion of the T and RH the aqueous solutions are not in thermodynamic equilibrium with the environmental conditions. Bulk pure water is not in equilibrium with the vapor conditions at any temperature, and would evaporate. The 5.09 M NaCl solution would be in equilibrium with the vapor only when the relative humidity is approximately 75%. At lower RH values it would tend to concentrate, and at still lower it would form a dry salt. At higher RH values, it would tend to form more dilute solutions. The 0.85 M NaCl solution is approximately in equilibrium with the 90% RH conditions. A solution, which is in equilibrium with the specified vapor, would form an aqueous solution at 109°C with some dissolved oxygen. With decreasing temperature (and hence, increasing RH) the solution will become more dilute, with a consequent rise in the dissolved oxygen content. At temperatures below 100°C the oxygen solubility curve would approximately follow the curve for the 0.85 M NaCl solution.

6.2.4 Determination of the Electrochemical Potential of Aqueous Solutions as a Function of Oxygen Partial Pressure or Equivalently Oxygen Solubility (TBD)

The electrochemical potential (eH) is a very strong determinant of the electrochemical corrosion processes that a metal alloy can be subjected to. Testing will be performed to determine the eH of relevant aqueous salt solutions under various relevant oxygen partial pressures and temperatures.

6.2.5 pH Control by the $\text{CO}_2 - \text{HCO}_3^- - \text{CO}_3^{2-}$ System (Stumm and Morgan 1981)

The pH of well J13-type waters is strongly influenced by the $\text{CO}_{2(aq)} - \text{HCO}_3^- - \text{CO}_3^{2-}$ system (bicarbonate/carbonate). The following chemical equations defined this system:



Ion balance requires that

$$[\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-]$$

and the equilibrium constant for water dissociation $[\text{H}_2\text{O}] \rightleftharpoons [\text{OH}^-][\text{H}^+]$ is given by

$$K_w = [\text{OH}^-][\text{H}^+].$$

Under some circumstances the partial pressure of gaseous carbon dioxide ($CO_{2(g)}$) will be very low because of the large partial pressure of water excluding air, which causes a loss of aqueous carbon dioxide, $CO_{2(aq)}$. The aqueous carbon dioxide will be replenished by recombination of the bicarbonate ion with the hydronium ion (eq. 2). By considering the ion balance and water dissociation equations, it can be shown that the pH of the solution increases as the partial pressure of carbon dioxide decreases.

6.2.6 Quantify the Dependence of the Aqueous Solution pH on the Partial Pressure of Carbon Dioxide as a Function of Temperature and Water Partial Pressure (TBD)

Experimental work and computer simulations will be performed to characterize the pH dependence of the aqueous solutions, especially under conditions of elevated temperatures and low carbon dioxide partial pressures. This work will be done to determine if very high pH solutions could form under expected repository conditions. Very high pH solutions may change the operative corrosion processes.

6.3 WATER ADSORPTION ON SURFACES IN THE ABSENCE OF HYGROSCOPIC SALTS

6.3.1 Water Adsorption on Flat Surfaces as a Function of Temperature and Relative Humidity

In the absence of hygroscopic salts, only limited amounts of water will adsorb on transition metal or metal oxide surfaces. The data of Lee and Staehle (1997) show that the amount of water adsorbed is somewhat independent of temperature, but is a function of relative humidity. (See Figures 4-1 and 4-2.) Estimates of water film thickness have been made from this data by assuming microscopically flat surfaces in their tests and a water density of 1g/cm^3 ; for the purposes of this analysis the assumptions are reasonable. Film thickness layers are of the order of 10–100Å.

It is important to note that bulk water condensation can occur only when $RH \geq 100\%$, that is, where the atmosphere is supersaturated with water vapor.

The adsorbed water layer may facilitate the electrochemical reduction of oxygen when it is present. Assuming a fixed partial pressure of oxygen, steady state amounts of oxygen in the films are expected because of the very thin thickness of the films and the fast diffusion of the oxygen in water.

6.3.2 Capillary Condensation as a Function of Relative Humidity and Temperature

The condensation of water vapor in crevices in contact with the metal barrier surfaces is of concern when considering corrosion under humid air conditions (see Table 6-1). The Kelvin equation is used to estimate the conditions under which water vapor condensation occurs in crevices in contact with the surface or in defects in corrosion products on the surface.

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Table 6-1. Calculation of the Radius of a Pore in which Water Condensation will Occur.
The Calculations were Performed using a Microsoft Excel Spreadsheet

	Pore radius, r , (Å) or (10^{-10} m)					
RH	100°C	80°C	70°C	60°C	50°C	40°C
0.99	710.2	786.5	827.6	871.2	917.1	965.3
0.98	353.3	391.3	411.7	433.4	456.2	480.2
0.97	234.3	259.5	273.1	287.5	302.6	318.5
0.96	174.8	193.6	203.8	214.5	225.8	237.7
0.95	139.2	154.1	162.2	170.7	179.7	189.1
0.94	115.4	127.8	134.4	141.5	149.0	156.8
0.93	98.4	108.9	114.6	120.7	127.0	133.7
0.92	85.6	94.8	99.8	105.0	110.5	116.4
0.91	75.7	83.8	88.2	92.8	97.7	102.9
0.90	67.7	75.0	78.9	83.1	87.5	92.1
0.85	43.9	48.6	51.2	53.9	56.7	59.7
0.80	32.0	35.4	37.3	39.2	41.3	43.5
0.75	24.8	27.5	28.9	30.4	32.0	33.7
0.70	20.0	22.2	23.3	24.5	25.8	27.2
0.65	16.6	18.3	19.3	20.3	21.4	22.5
0.60	14.0	15.5	16.3	17.1	18.0	19.0
0.55	11.9	13.2	13.9	14.6	15.4	16.2
0.50	10.3	11.4	12.0	12.6	13.3	14.0
0.45	8.9	9.9	10.4	11.0	11.5	12.1
0.40	7.8	8.6	9.1	9.6	10.1	10.6
0.35	6.8	7.5	7.9	8.3	8.8	9.2
0.30	5.9	6.6	6.9	7.3	7.7	8.1
0.25	5.1	5.7	6.0	6.3	6.6	7.0
0.20	4.4	4.9	5.2	5.4	5.7	6.0
0.15	3.8	4.2	4.4	4.6	4.9	5.1
0.10	3.1	3.4	3.6	3.8	4.0	4.2

The relative humidity at which condensation occurs in a pore of radius r is given by Fyfe (1994):

$$x_{RH} = \exp(P_c MW_{H_2O} / \rho RT) \text{ with } P_c = 2\gamma/r.$$

Rearranging the equation to define the radius as a function of temperature and relative humidity gives:

$$r = -2\gamma MW / (\rho RT \times \ln(x_{RH}))$$

where

x_{RH} fractional relative humidity

MW_{H_2O} molecular weight (kg/mole)

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ρ	mass density of water (kg/m ³)
R	gas constant (8.31433 joules/K-mole) (Weast and Astle 1981)
γ	surface tension of water-air (joules/m ²)
T	temperature (K).

Sample calculation for $T = 353.15$ K (80°C) and $x_{RH} = 0.91$.

$$r = -2 \cdot 0.0626 \text{ joules/m}^2 \cdot (18.0153/1000)/0.97183 \text{ gm/cm}^3 \cdot (1 \text{ kg}/1000 \text{ gm}) \cdot (1000000 \text{ cm}^3/\text{m}^3) \cdot (8.31433 \text{ joules/K-mole}) \cdot 353.15 \text{ K} \cdot \ln(0.91)$$

$$r = 8.38 \times 10^{-9} \text{ meters.}$$

6.3.3 Relative Humidity Effect on the Oxidation (TBD) and Dissolution of the Candidate Materials

The limited amount of water in the films due to adsorption under $RH < 100\%$ is not sufficient to support a significant amount of dissolution of the candidate materials because of the very limited solubility of these material in near-neutral waters.

The oxidation of materials may be enhanced at high relative humidity because of the enhancement of the reduction of oxygen due to the adsorbed water film. Under these conditions the oxidation is expected to be controlled by the solid-state diffusion of ions through the oxide layer, just as it would be for dry oxidation. The adsorbed water film may contribute to the electrical potential across the oxide, which affects the ion diffusion. The extent of this enhancement will be investigated, but presently, it is not considered to be significant at the oxygen partial pressure expected.

6.4 AQUEOUS SALT SOLUTIONS ON THE DSs AND WPOBs

Aqueous solutions of hygroscopic salts on the DSs and WPOBs can occur as a result of several processes. The hygroscopic salts enable aqueous solutions to exist at relative humidities below 100%. Hygroscopic salts may be deposited by aerosols and dust, and may be introduced with the backfill. They will be contained in the seepage water that enters the drifts and the episodic water that flows through the drifts.

If the salts are deposited under very low relative humidity conditions, then the aqueous solutions will form after the relative humidity exceeds the deliquescence point for the salt mixture present. At the deliquescence point, the solutions are very concentrated and may only consist of specific ions in the salt mixture. As the relative humidity increases the solutions will become more dilute and other ions in the salt mixture may become soluble.

If the salts contact the components as a result of seepage or episodic water flow at moderate to high relative humidity, then the aqueous solutions may result from the evaporative/boiling concentration of the solutions. The amount of concentration and precipitate formation depends

on the relative humidity and temperature differences between the aqueous solution and the specific component.

It is possible that the temperature and relative humidity differences between the incoming water the engineered barrier system (EBS) component may be such that aqueous solutions will exist on the component under T and RH conditions that do not support those solutions. For example, ions may be in solution that would be expected to form precipitates. The extent and consequences of this are being investigated.

Sections 6.4.1–6.4.3 contain offer a basic understanding for the aqueous salt solutions that may form on the DSs and WPOBs, then discuss the experimental work that has been performed to date, and is ongoing.

6.4.1 Deliquescence Points and Boiling Points for Pure Salts

As stated in Section 6.1, it is the deliquescence point of a particular salt that defines the RH condition necessary for aqueous electrochemical corrosion processes of a metal with salt deposits to occur at a given temperature. Similarly, salt mixtures will have a characteristic deliquescence point that is dependent on the ions in the mixture.

The deliquescence points have been determined for a limited number of pure salts over a limited temperature range (Greenspan 1977). The data for various pure salts given in Table 4-8 are plotted in Figure 6-6. Included in the figure are plots for the maximum *RH* obtainable for pure water with atmospheric conditions such that boiling points are 96°C ($P_{total} = 87.67$ kPa) and 100°C ($P_{total} = 101.32$ kPa). Also included in the figure are the boiling points at sea level ($P_{total} = 101.32$ kPa) for some salts (Frazier 1928).

The boiling point for an aqueous salt solution is the temperature at which the equilibrium water vapor pressure of the salt solution is equal to the atmospheric pressure. The aqueous salt solution concentration is also at its maximum. Hence the *RH* value at the boiling point is its deliquescence point.

For pure salts whose solubilities change little with temperature, the deliquescence points also change little with temperature. For instance, NaCl, whose solubility changes from 35 gm/100 cm³ of water @ 20°C to 37 gm/100 cm³ of water @ 100°C (see Table 4-8), the deliquescence points are nearly constant with temperature (72%–75% RH). At the boiling point of NaCl the RH is 73.15%. Similar behavior is seen for KCl and K₂SO₄.

In contrast, for pure salts whose solubility changes significantly with temperature, the deliquescence points also change significantly with temperature. For instance, NaNO₃, whose solubility changes from 97 gm/100 cm³ of water @ 20°C to 197 gm/100 cm³ of water @ 100°C (see Table 4-8), the deliquescence changes significantly with temperature from 85% @ 20°C to 70 @ 90°C. At the sea-level boiling point (120.6°C), the RH is 50.1%.

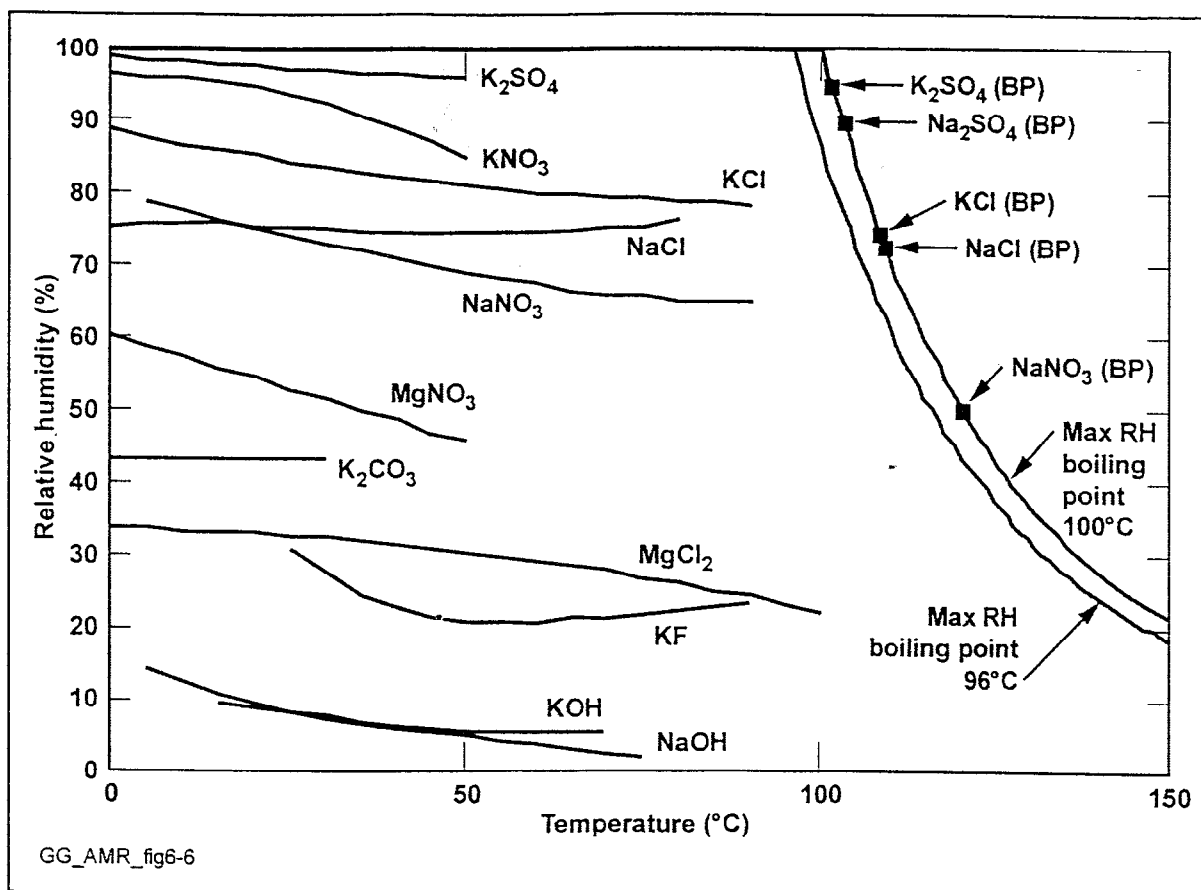


Figure 6-6. Deliquescence Points (Greenspan 1976) and Boiling Points for Several Pure Salts (Frazier 1928)

6.4.2 RH Effect on Aqueous Solution Composition

Decreasing the relative humidity of the atmosphere in contact with an aqueous solution of a pure salt will lead to the evaporative concentrating of the aqueous solution. Decreasing the RH below a certain value (the deliquescence point) will result in the precipitation of the salt. This process is illustrated in Figure 6-7.

For mixed salt solutions, decreasing the relative humidity of the atmosphere will concentrate some of the ion in solution and cause the precipitation of some species. For instance, as discussed below, the initial concentrating of J13 water causes the precipitation of calcium and magnesium species.

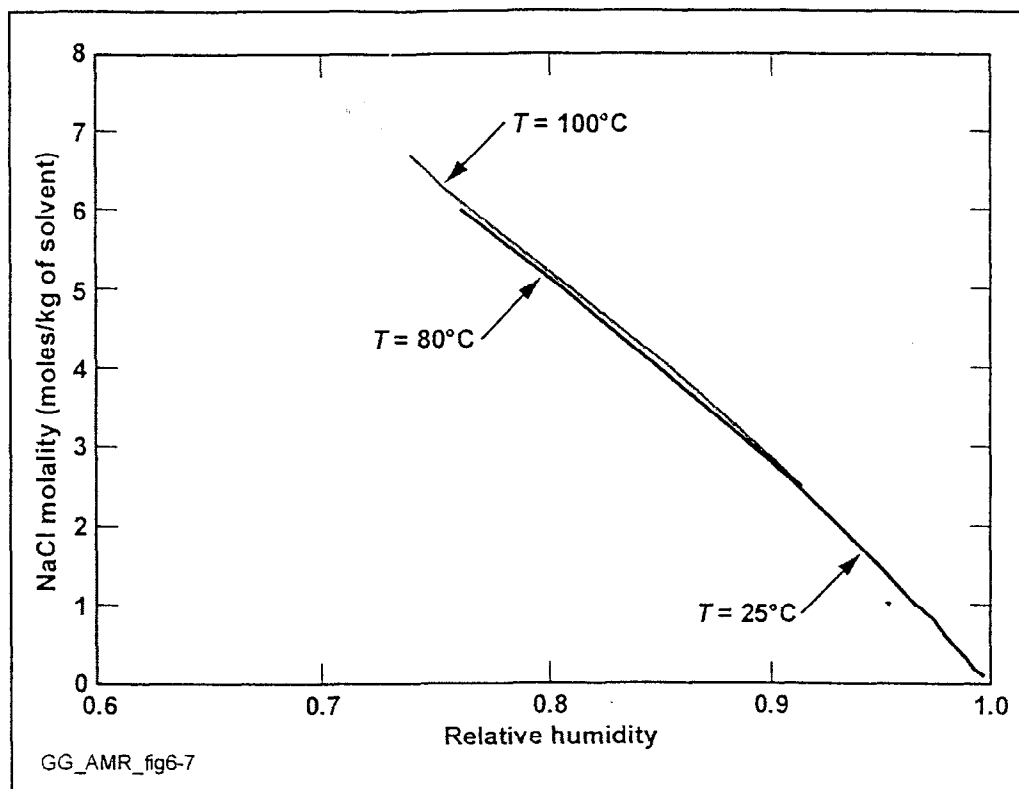


Figure 6-7. Aqueous NaCl Molality as a Function of Fractional Relative Humidity (Frazier 1928)

6.4.3 Regions of Concern for the Aqueous Corrosion of DSs and WPOBs

The DSs and WPOBs are expected to be most susceptible to electrochemical corrosion processes for temperatures above 80–85°C. The temperature range of interest may extend to temperatures up to 120–125°C; this uncertainty is due to the boiling point of NaNO_3 solutions. The discussion above indicates that due to the temperature dependence of solute solubility and the concentration dependence on relative humidity, multiple compositions and concentrations as a function of temperature may be of interest for their effects on the corrosion susceptibility of DSs and WPOBs.

6.5 BOILING/EVAPORATIVE CONCENTRATING OF SIMULATED WELL J13 WATER

The testing program has chosen to use well J13 water as a reference for waters that may contact the DSs and WPOBs. If a different composition of water is later deemed more appropriate, then an analysis will be performed to determine if that composition has a significant effect on the results presented in this section.

As discussed in Section 6.4, it is inevitable that the waters in contact with the DSs and the WPOBs will be more concentrated than the ambient waters at Yucca Mountain or the seepage water that enters the drifts. Several tests are ongoing to characterize the changes that occur upon boiling/evaporative concentrating of simulated well J13 and simulated slightly concentrated well

J13 water. These tests include the evaporative concentrating of simulated well J13 water that is dripped onto heated crushed tuff that is at or near the boiling point of the concentrated solution, and evaporative concentrating of simulated well J13 water that is dripped onto crushed tuff under conditions of constant temperature and relative humidity.

6.5.1 Initial Concentrating of Well J13 Water

It is expected that the initial concentrating of well J13 water will lead to the precipitation of Ca- and Mg-based salts/minerals because of the very low solubility of the Ca and Mg in high bicarbonate/carbonate waters in neutral/alkaline aqueous solutions (See Section 4.1.8). The composition of well J13 water is given in Table 4-13. The largest anionic component of the water is the carbonate/bicarbonate couple (total bicarbonate concentration of 148 ppm). Calcium and magnesium concentrations are 13 and 2 ppm respectively. Evaporative concentrating of the aqueous solutions will exceed the solubility limits for the calcium and magnesium carbonates. The removal of Mg and Ca ions from solution by concentrating simulated well J13 waters has been documented experimentally (see Section 6.5.2). The magnesium seems to be removed to a greater extent than the calcium; however both are removed to a much greater extent than the Na and K ions. In the discussions that follow particular emphasis is placed on the water chemistry of sodium (Na) and potassium (K) salts because these are expected to be the dominant cation species.

6.5.2 Evaporative Concentrating of a Simulated Well J13 by Boiling

The results of this testing are presented in Section 4.1.17. The following figures are plots of a concentration factor defined as the ratio of the concentration in the solution to the concentration in the initial solution. The concentration factor for the cations is shown in Figure 6-8. As expected, the Na^+ and K^+ ion concentrations are continuously increasing in the solution. Also as expected, the Mg^{2+} and Ca^{2+} ion concentrations are very low. The one high value for Ca^{2+} that occurred in the first sampling does not persist at the later samplings.

The concentration factors for the anions show some interesting trends with continued concentration (see Figure 6-9). The Cl^- and NO_3^- concentrations are continuously increasing with sampling. The F^- concentration appears to be approaching very small values with increasing concentration. The SO_4^- concentration, while initially increasing with the Cl^- and NO_3^- concentrations, appears to be remaining constant or decreasing with concentrating.

6.5.2.1 Determination of the pH of the Highly Concentrated Elevated Temperature Solutions (TBD)

The in situ determination of the pH of highly concentrated solutions at elevated temperatures is required to fully characterize the solutions. Specialized electrodes are required.

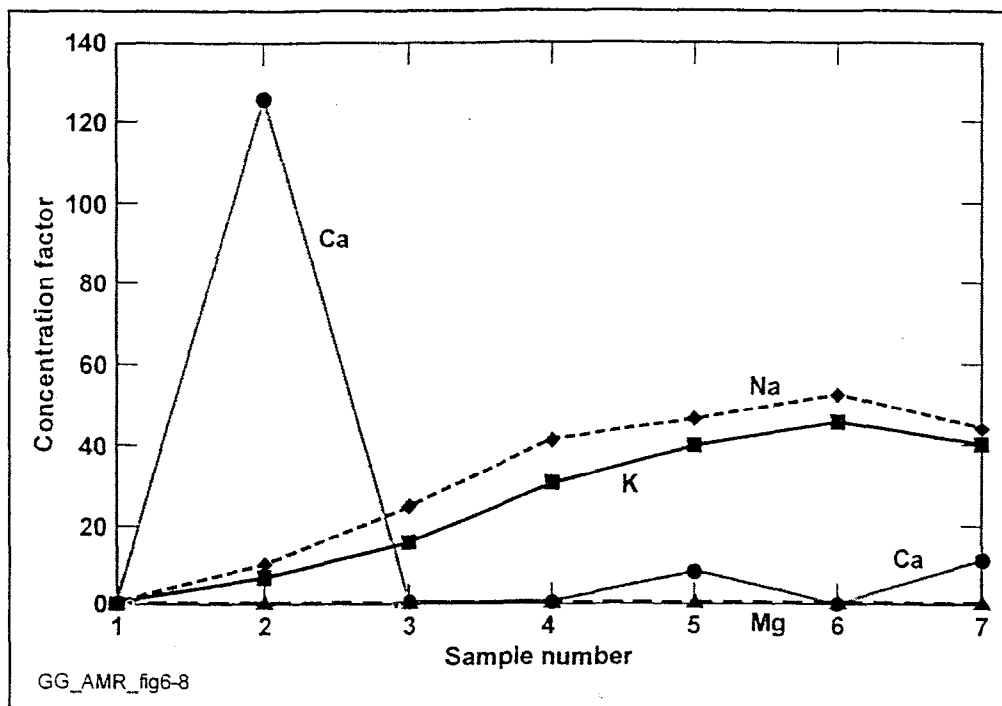


Figure 6-8. Concentration Factors for the Cations for the Evaporative Concentration of Simulated Well J13 Water Near the Boiling Point.

The First Sample Corresponds to the Initial Solution. Data in Section 4.1.17

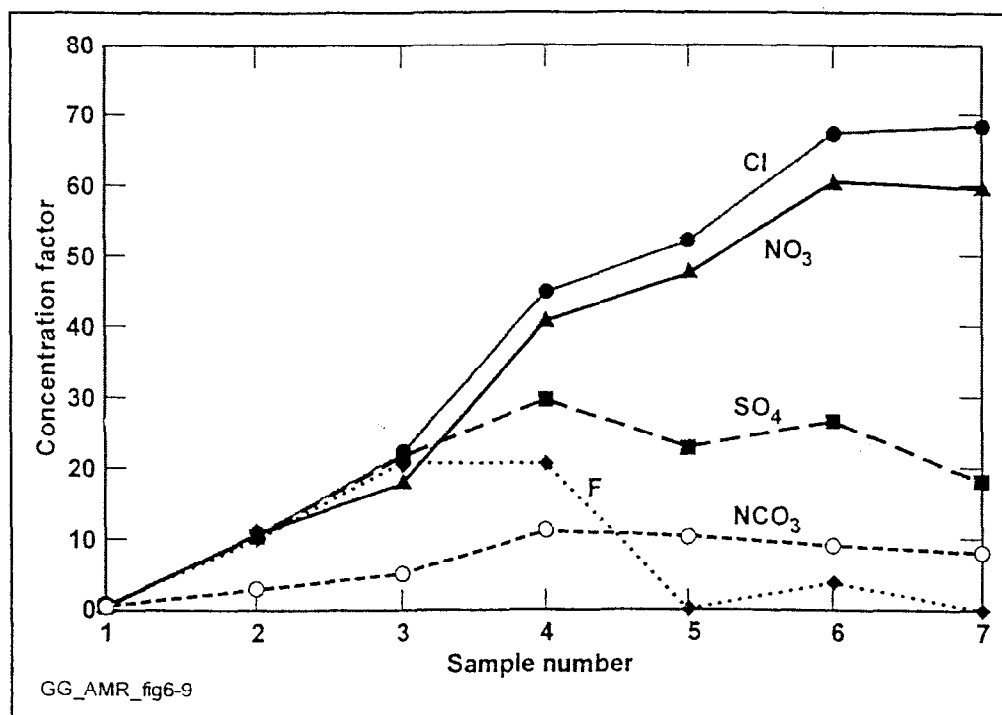


Figure 6-9. Concentration Factors for the Anions for the Evaporative Concentration of Simulated Well J13 Water Near the Boiling Point.

The First Sample Corresponds to the Initial Solution. Data in Section 4.1.17

6.5.3 Water Composition as a Function of Relative Humidity at Fixed Temperatures (DTN #LL990703005924.083 and TBD#)

The objective of this work is to characterize the waters that would result from the evaporative concentration of waters contacting the WPOBs and the DSs in the range of temperature/relative humidity where candidate materials might be susceptible to corrosion. Testing has begun at 90°C and will continue at regular temperature intervals. The results are reported for evaporation at 85% RH. The starting solution was simulated 100-times concentrated well J13 water. The aqueous solution dripped through a column of crushed tuff and collected in a beaker at the outlet of the column. Additional evaporation of the aqueous solution occurred in the beaker.

In Table 6-2 a concentration factor, which is the ratio of a specific ion concentration of the sample solution to the specific ion concentration of the initial solution, is presented. The data show that under these conditions calcium, magnesium, bicarbonate (as an indicator of total carbonate) and possibly fluoride are not concentrated to the extent that chloride, nitrate, sulfate, sodium, and potassium are. This result is consistent with the expected precipitation of carbonate species, and with the initial precipitation of some fluoride-containing salts/minerals.

Table 6-2. Results of the Evaporative Concentration of Simulated Well J13 Water Under Conditions of Constant Temperature and Relative Humidity

Species	Starting Sol'n (mg/liter)	Final Sol'n 85%RH/90°C (mg/liter)	Concentration Factor
Sample #	Initial J13 Batch A	J13-01	
DTN #LL990703005924.083			
Cl		15200	21.8
NO ₃		14600	20.7
SO ₄		30400	19.3
F		3500	18.1
HCO ₃ [*]		11370	14.4
Na		79700	20.2
K		10020	19.4
Ca		26	4.5
Mg		0	0

*Total inorganic carbon expressed as bicarbonate.

6.5.4 Salts/Minerals Formed Due to Evaporation of a Simulated J13 Water (TBD)

Identification of salt/mineral phases, which result from the evaporative drying of simulated J13 water, will be performed on the precipitates that formed during the evaporative/boiling concentration testing. This will give an indication of the scale-forming minerals. They will also give an indication of the solutions that may form after the relative humidity increases above the deliquescence point of the salt mixtures.

6.6 THE EXISTENCE OF AQUEOUS SOLUTIONS ON THE EBS COMPONENTS UNDER ENVIRONMENT CONDITIONS THAT DO NOT SUPPORT THOSE SOLUTIONS (TBD)

Aqueous solutions may exist on the EBS components where the evaporation rate is slower than the seepage flow of additional water. Under these conditions aqueous solutions may exist at higher temperatures or lower relative humidities than would normally support those solutions. The extent to which this may occur is being investigated to understand if there would be an increase in the aggressiveness of the aqueous solutions contacting the EBS components.

6.7 ESTIMATE OF THE COMPOSITION OF CORROSIVELY AGGRESSIVE AQUEOUS SOLUTION THAT COULD RESULT FROM CONCENTRATING YUCCA MOUNTAIN WATERS

To estimate the upper bound for the boiling point of waters that might contact the DSs and WPOBs surfaces the following scenario is postulated. In the near field, refluxing of water along the fractures will result in the chromatographic separation of the salts by their hygroscopic and solubility characteristics. That is, the salts will separate with the most soluble and hygroscopic salts migrating to the regions of lowest relative humidity, while the least soluble and hygroscopic will remain in the regions of highest relative humidity.

In terms of the salts present in the waters at Yucca Mountain, it is expected that the chloride and nitrate salts of sodium and potassium are the most likely to be the most soluble and hygroscopic salts remaining in solution upon concentrating Yucca Mountain type water. During the initial concentrating of the Yucca Mountain water, the calcium and magnesium ions are expected to form rather insoluble carbonate and silicate precipitates. With the calcium and magnesium ions removed from solution, it is the chloride, fluoride, sulfate, and nitrate salts of sodium and potassium that will remain in solution. As shown in Table 4-9, NaF has very limited solubility, and the sulfate salts of Na and K have also have limited solubilities.

It is expected that further concentration of the aqueous solution would ultimately result in nitrate-based solution with small amounts of other ions, most notably the chloride ions. In order for the solution to remain aggressive toward corrosion, it was decided that the solution, in addition to being a high-temperature boiling solution, must also contain an aggressive ion, such as chloride. It was decided that the aggressive high boiling solution would be a mixture of chloride and nitrate salts of potassium and sodium.

At 100°C, the solution was made by formulating a saturated solution of NaNO_3 , and then adding an additional amount of KCl. The amount of KCl added corresponded to a Cl ion concentration of 3.6 M. Similarly, at 120°C, the solution was made by increasing the NaCO_3 nearly to its saturation limit, and then adding the amount of KCl that produces a Cl ion concentration of 4.3 M.

6.8 CHARACTERIZATION OF MINERAL/SALT SCALE FORMATION ON METAL SURFACES (TBD)

The predominant scale-formers in Yucca Mountain type waters are calcium carbonate and silica (Cowan and Weintritt 1976). The tendency for carbonate scale formation is greatly enhanced by

the concentration of the ions by water evaporation, provided the aqueous solution remains alkaline. Silica deposition will also be enhanced by water evaporation, provided that the solution's pH does not reach alkaline values where the silica solubility is greatly enhanced.

Scale can protect the underlying material if it forms a dense adherent layer. However, scale can have a deleterious effect on the underlying material if it forms a porous layer or a crevice with the underlying material.

The objective of this study is to characterize the scale that forms on the candidate materials for the DS and the WPOB under conditions simulating the repository environment.

7. CONCLUSIONS

The major cations in Yucca Mountain waters are sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), and silicon (Si). The major anions in Yucca Mountain water are chloride (Cl), fluoride (F), nitrate (NO₃), sulfate (SO₄), and bicarbonate (HCO₃)/carbonate (CO₃).

Using published information, it was shown that if aqueous solutions are present above the boiling point of pure water (due to hygroscopic salts), then the presence of oxygen partial pressure results in dissolved oxygen. The amount of dissolved oxygen affects the electrochemical potential, Eh, which in turn is a determinant of electrochemical corrosion processes.

Under conditions of very low partial pressure of CO_{2(g)}, bicarbonate/carbonate waters can obtain very high pH values. A consequence of the high pH conditions is the very high solubility of silica. This was seen under laboratory conditions. Whether the conditions necessary for the formation of the high-pH solutions are operable under potential repository conditions needs further investigation.

Experimental studies show that the initial concentrating of the waters causes Ca and Mg precipitates to form. Effectively, the solutions are then chloride, fluoride, nitrate, sulfate, and bicarbonate/carbonate salts of sodium and potassium. Further concentrating these waters removes the fluoride ions from solution and decreases the sulfate concentration relative to the chloride and nitrate. The maximum boiling points of the concentrated solutions to date is 108°C.

The characteristics of the aqueous solutions that are in contact with the EBS components, DSs, and WPOBs depend upon the temperature of the component, the relative humidity of the air at the component, and nature of the hygroscopic salts deposited on the component. The most prevalent hygroscopic salts expected to be deposited on the EBS components are nitrate salts of potassium and sodium. The solubilities of both salts are strongly temperature-dependent, which effects the hygroscopic properties of these salts. In particular, their decreasing solubility with temperature indicates an increasing deliquescence point with decreasing temperature. Experimental work is in progress to characterize the nature of the hygroscopic salts in this temperature/relative humidity region.

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9. ATTACHMENTS

Attachments to this document are listed in Table 9-1.

Table 9-1. List of Attachments

Attachment Number	Description	Size
I		
II		
III		
IV		
V		
VI		
VII		
VIII		
IX		
X		

The following supporting documents are in electronic form on a CD-ROM. Each file is identified by it's name, size (in bytes), and the date and time of last access.

DOS Filename byte size date time WIN95 filename

